

Cation and Water Content Effects on Dipole Rotation Activation Energy of Smectites

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ABSTRACT

In soil science, single frequency permittivity measurements are used to determine soil water content, and single frequency bulk electrical conductivity is used to determine soil salinity. The accuracy of these measurements may be influenced by complex interactions between frequency, temperature, and water that is tightly bound to clay surfaces. The purpose of this study is to determine the effect of temperature, saturating cation, water content, smectite properties, and frequency on electrical properties of humidified clays by analyzing three different activation energies for dipole rotations, which are calculated from the temperature dependence of electrical properties. Four reference smectites saturated with K, Na, Ca, and Mg and equilibrated at relative humidities ranging from 56 to 99% were investigated over a frequency range from 3×10^5 to 1×10^9 Hz. Two of the three activation energies were found to decrease slightly as water content increased. Higher activation energies were found for smectites saturated with Mg and K and lower values for smectites saturated with Na and Ca. Trends for type of clay were variable but appeared to be influenced by both the total water content and the distribution of water between the interlayers and the external surfaces of the smectite quasi-crystals. Changes in quasi-crystal orientation induced by thermal cycling were also found to influence the activation energies. The results indicate complex frequency and temperature dependent interactions impact electrical properties of the clays. We conclude that no simple equation will correct for temperature and clay content effects on single frequency measurements of permittivity or bulk electrical conductivity.

Electrical Spectra

IN MATERIAL SCIENCE, frequency-dependent electrical spectra are used for characterizing properties of materials, but in soil science the emphasis has been on single-frequency measurements. Time domain reflectometry (TDR), capacitance probes, and impedance probes are commonly used to determine the water content of soil. A four-electrode Wenner device is a standard for in situ electrical conductivity measurements (Hendrickx et al., 2002), but often TDR is also used for bulk electrical conductivity measurements. Bulk electrical conductivity measurements are used to determine soil salinity. However, recent evidence indicates that the electrical properties of soils high in smectites are also influenced by complex interactions involving water associated with clay surfaces (Saarenketo, 1998; Nadler, 1998, 1999; Logsdon, 2000). Therefore, a more rigorous understanding of the complex electrical properties of smectites is necessary to more accurately estimate soil water content and salinity using soil electrical properties.

An applied electrical field causes both the movement

of charge carriers and the alignment of dipolar molecules (Jonscher, 1996; Baker-Jarvis, 2000). When the electrical field is removed, the molecules reorient back to a more stable arrangement, with a time lag. The time lag of reorientation or relaxation varies as a function of frequency for alternating electrical fields. Molecular relaxation of some materials is inter-dependent because the reorientation of one molecule changes the local electrical field of the neighboring molecules. Furthermore, both relaxation and charge-carrier-movement occur in jumps across activation energy barriers. The magnitude of these activation energy barriers provides information about the nature of the material.

The complex electrical properties of a material have both real and imaginary components. The electrical properties may be expressed as the complex, frequency-dependent electrical conductivity, $\sigma^*(f)$, which emphasizes hopping charge carriers; or they may be expressed as the complex frequency dependent relative permittivity, $\epsilon^*(f)$, which emphasizes molecular polarization and charge storage (Anis and Jonscher, 1993). The $\sigma^*(f)$ and $\epsilon^*(f)$ are interrelated

$$\sigma^*(f) = i2\pi\epsilon^*(f)\epsilon_v \quad [1]$$

where ϵ_v is permittivity of a vacuum = 8.854×10^{-12} F m⁻¹.

Movement of charge carriers can also contribute to polarization and relaxation of macromolecules at low frequencies. The low frequency dispersion phenomena contribute to permittivity of humidified samples (Dissado and Hill, 1984; Jonscher, 1996), and are due to proton hopping along surfaces. The result is charge separation within the volume of a particle that changes polarity for low frequencies of alternating electrical field. The low frequency dispersion has been observed for many hydrated materials, including soil, sand, and clay (Dissado and Hill, 1984; Anis and Jonscher, 1993; Logsdon and Laird, 2003).

Various empirical equations have been used to reduce electrical spectra to a few fitted parameters (Moynihan, 1994; Kuang and Nelson, 1998). For example, the complex electrical conductivity spectra can be described by the empirical equation

$$\sigma^*(f) = \sigma_0(1 + f/f_r)^n \quad [2]$$

where σ_0 is the direct current electrical conductivity, f_r is the frequency corresponding to the change in slope (also known as the relaxation frequency), and n is the log slope at the higher frequency end (Jonscher, 1983). The relaxation frequency is an important fitted parameter for electrical properties of materials, which relates to dipole rotation.

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Abbreviations: RH, relative humidities; TDR, time domain reflectometry.

Temperature Effects

Free water, water that is not bound to colloids, shows a slight decrease in relative permittivity with increasing temperature (Stogryn, 1971); by contrast, soils high in smectite clays have increasing relative apparent permittivity with increasing temperature (Wraith and Or, 1999; Logsdon, 2000). The positive temperature effect is dependent on the high bulk electrical conductivity of these soils (Persson and Berndtsson, 1998; Logsdon, 2000; Robinson et al., 2003).

Obtaining electrical spectra at different temperatures allows calculation of three different activation energies. The activation energy due to electrical conductivity (E_p), can be determined from the apparent σ_0 ,

$$\ln(\sigma_0 T) = X - E_p/(RT) \quad [3]$$

where T is absolute temperature, R is the universal gas constant, and X is the fitted intercept (Simon and Flesch, 1999). This E_p is the largest barrier for percolation of charge carriers between the electrodes (Dyre, 1991).

The second activation energy is determined from the relaxation time or frequency, and we will call it the activation energy due to dipole rotation (E_r). To determine E_r , we must first determine the free energy of activation for dipole rotation (ΔG_r) at each temperature from (Glasstone et al., 1941)

$$\Delta G_r = RT \ln[kT/(2\pi f_r h)] \quad [4]$$

where k is Boltzman's constant, h is Plank's constant, and the other symbols are as defined above. Then from

$$\Delta G_r = \Delta H_r - T\Delta S_r \quad [5]$$

we determine the change in enthalpy (ΔH_r is considered equivalent to activation energy, E_r). The ΔS_r is the change in entropy for the system.

The third activation energy was described by van Turnhout and Wübbenhorst (2002) as an apparent landscape activation energy (E_{app}) and is determined from

$$E_{app}(f, T) = -RT^2 \frac{\partial \epsilon''/\partial T}{\partial \epsilon''/\partial \ln f} \quad [6]$$

where ϵ'' is the imaginary component of the complex frequency dependent relative permittivity and other symbols are defined above. Procedurally, the first step is to determine the local slope of ϵ'' as a function of f and separately as a function of T , then the ratio of these slopes for each combination of f and T is used in Eq. [6] to determine E_{app} . This necessarily excludes the end values. The apparent landscape activation energy indicates the activation energy for molecular dipole rotation at the specific temperature and frequency. Any of the electrical property variables could be substituted for ϵ'' , such as ϵ' , σ' , or σ'' (van Turnhout and Wübbenhorst, 2002). For many materials, the change in ϵ'' as a function of f and T is due to molecular dipole rotation and associated relaxation (reorientation) under an applied electrical field. Using ϵ'' in Eq. [6] may enable us to see other temperature effects, such as thermal expansion or a change in entropy (van Turnhout and Wübbenhorst, 2002).

The specific objectives of this study were to determine temperature effects on dielectric and electrical conductivity spectra of reference smectites, to use the temperature effects to determine three types of activation energies, and to evaluate the effect of saturating cation, water content, and smectite mineralogy on these activation energies.

MATERIALS AND METHODS

The preparation and analysis of the four reference smectites (Table 1) used in this study are described in Logsdon and Laird (2004). The four smectites have different surface charge densities and fraction of charge in tetrahedral sites. To prepare the reference clays, the raw clay ore was first dispersed in deionized water by stirring, and the clay fraction ($<2\text{-}\mu\text{m}$ equivalent spherical diameter) was separated by sedimentation. The clay fraction was washed three times with 1 M salt solution of CaCl_2 , MgCl_2 , NaCl , or KCl dialyzed against deionized water, and finally freeze-dried. Total chemical analysis was done for each of the cation saturated $<2\text{-}\mu\text{m}$ smectite samples using suspension nebulization-ICP-AES (Laird et al., 1991). The results were interpreted using procedures outlined by Gast (1977) to determine cation exchange capacity, surface charge density, percentage of tetrahedral charge, and specific surface area.

The Ca-, Mg-, Na-, or K-saturated smectites were equilibrated in desiccators over saturated salt solutions [deionized water, ZnSO_4 , NH_4Cl , and $\text{Mg}(\text{NO}_3)_2$], which stabilized the room temperature relative humidities (RH) at 99, 85, 74, or 56%. After equilibration at each RH, duplicate samples were each packed into a truncated coaxial cell (Logsdon and Laird, 2004). When the packing densities varied excessively between the duplicates, another sample was prepared and measured. After the humidified clay was packed into the cell, the cell was sealed to prevent loss of water during measurement. We used a vector network analyzer (Agilent 8753E) to make reflection measurements after calibration with open, short, and load standards. We determined S11 values at six temperatures between 10 and 35°C for each sample at 800 frequencies between 300 kHz and 3 GHz. The measurements at descending temperatures were followed by measurement at ascending temperatures. The complex S11 values were used to determine complex impedance. The complex impedance was converted to σ^* and permittivity (ϵ^*) as described in Campbell (1990) and Logsdon and Laird (2002). The electrical length of the sample holder was back-fitted as described in Heimovaara et al. (1996).

For this study we were primarily concerned with the real component of electrical conductivity, σ' , although the imaginary component, σ'' , is useful for differentiating electrode polarization (charges that build up at the electrodes and increase measured ϵ^* at low frequencies, Schwan, 1966).

Calculations

We fit σ_0 , f_r , and n from $\sigma'(f)$ using Eq. [2] for $f < 500$ MHz. The data were fit in SAS (1988) using the NLIN procedure with the Marquardt algorithm. For all the samples we calculated electrical conductivity activation energies from Eq. [3], and dipole rotation activation energies (E_r) from Eq. [4] and [5].

We calculated landscape activation energies from Eq. [6] using ϵ'' because the data were less noisy than the real compo-

Table 1. Properties of the studied smectites.

Clay	CEC [†]	SCD [‡]	SA [¶]	TC [#]
	cmol, kg ⁻¹	$\mu\text{mol, g}^{-1}$	m ² g ⁻¹	%
Hectorite	88	1.20	751	0
SPV Bentonite	96	1.28	752	8
Otay	109	2.11	584	26
IMV Bentonite	122	1.70	752	20

[†] CEC is cation exchange capacity.

[‡] SCD is surface charge density.

[¶] SA is specific surface area.

[#] TC is percent tetrahedral charge.

nent of dielectric, ϵ' , or the real or imaginary components of σ . Because we started with 800 points for f , we determined slopes for every 10 points of $\ln(f)$, and determined mean values of ϵ'' at each corresponding $\ln(f)$. Then we determined local slopes for each of the internal temperatures, for each mean $\ln(f)$. The ratios of these slopes at each mean $\ln(f)$ and T were used in Eq. [6] to determine E_{app} . Because of minimal change with frequency <200 MHz, the set of data up to 200 MHz were averaged. For statistical comparisons, values for 20 and 25°C were averaged because they represented the mid temperature range where the procedure was more reliable. We also examined the trends of E_{app} as a function of temperature using linear correlation analysis, separately for ascending and descending temperatures. Across all samples for each of the calculated activation energies, we used analysis of variance (GLM procedure, SAS, 1988) to determine significant differences in main effects (cation, clay).

RESULTS AND DISCUSSION

Example for a Single Sample

Because of the large volume of data, we first present examples from a single sample (Mg, IMV, 85% humidity or water content $0.347 \text{ m}^3 \text{ m}^{-3}$) to show the type of patterns apparent as a function of temperature. The σ' showed frequency-dependence over a small frequency range (Fig. 1a). Upward curvature of σ'' at low frequen-

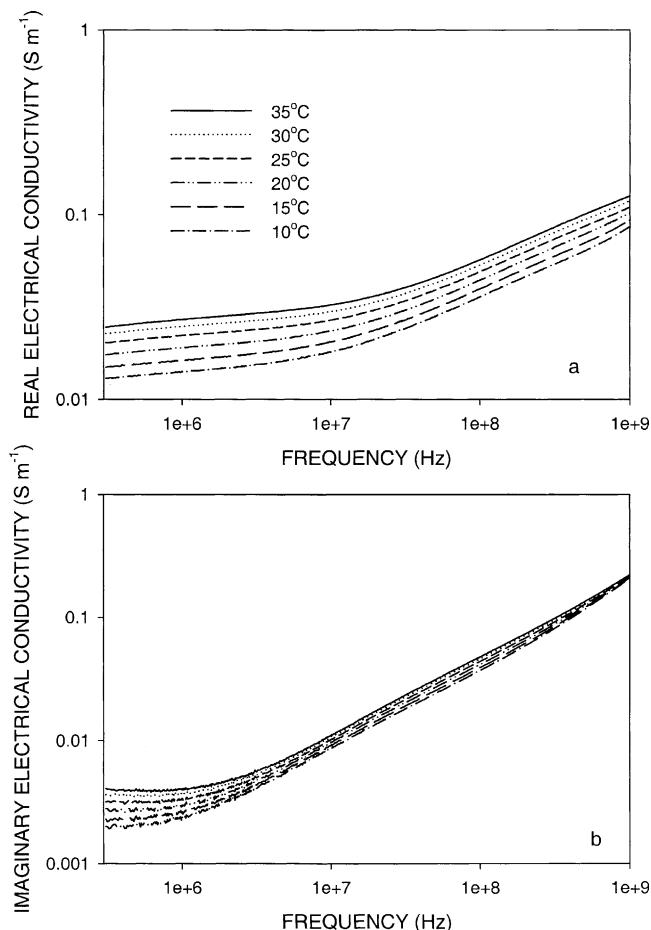


Fig. 1. Example of the (a) real and (b) imaginary components of the electrical conductivity spectra for Mg-IMV at 85% relative humidity (water content $0.347 \text{ m}^3 \text{ m}^{-3}$), showing the frequency-dependence.

cies (<500 MHz) (Fig. 1b) indicated electrode polarization for the warmer samples. In general for all the samples, electrode polarization was most evident for the warmer and wetter samples (not shown).

The E_{app} was generally constant as a function of frequency below 2×10^8 Hz (Fig. 2). When the temperature of the example sample decreased, the E_{app} increased (Fig. 2a); when the temperature increased, there was still a small increase in E_{app} (Fig. 2b). Most of the samples showed the same constancy of E_{app} at the lower frequencies, although a few of the wetter samples showed an initial increase, a peak, and a decline at high frequencies (Fig. 3b). Some of the drier samples showed a decline with increasing frequency, but the rate of decline was greater for the higher frequencies (Fig. 3a).

The E_{app} can be used to help explain electrical processes in a system (van Turnhout and Wübbenhorst, 2002). If E_{app} is constant with temperature, then the process follows Arrhenius law

$$\tau_R(T) = \tau_\infty \exp[E_a/(RT)] \quad [7]$$

in which τ_r is relaxation time $[= 1/(2\pi f_r)]$, τ_∞ is the prefactor time, and E_a is an activation energy. For the descending temperatures of all of our samples, 45% showed that E_{app} increased with decreasing temperatures ($P = 0.05$), and 55% did not change significantly with temperature. For the ascending temperature analysis, 20% of our samples showed increasing E_{app} with increasing tem-

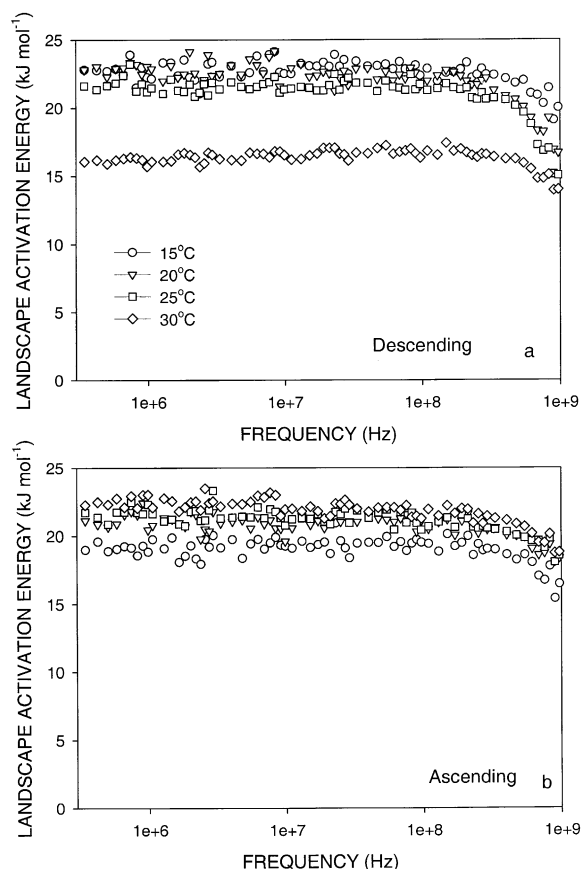


Fig. 2. Example of landscape activation energy as a function of frequency and (a) decreasing or (b) increasing temperature for Mg-IMV at 85% relative humidity (water content $0.347 \text{ m}^3 \text{ m}^{-3}$).

peratures, and 80% did not change significantly with temperature. If the system is controlled by Debye relaxation processes (molecular dipole rotation), then E_{app}/T should be constant as a function of temperature. Only 5% of our samples showed constant E_{app}/T for descending temperatures and 4% of our samples showed constant E_{app}/T for ascending temperatures. All the rest showed a ratio that decreased significantly as temperature increased. This indicated that typical molecular dipole rotation was not a major component of the response for our data.

A possible mechanism for our humidified smectites could be increased entropy that developed slowly after the sample was packed into the coaxial cell. The packing undoubtedly introduced some preferred orientation of the very anisotropic smectite quasi-crystals. Thermal expansion and contraction as well as changes in crystalline swelling (Kittrick, 1969) caused by cooling and heating treatments, reoriented the quasi-crystal and increased entropy in the system. An entropy-driven process could be the reason that E_{app} increased both during the initial cooling treatment and during the subsequent heating treatment. In natural environments, surface soils are subject to repeated diurnal cooling and heating cycles.

Effect of Cation and Smectite Type

When averaged across clays and water contents, the activation energies showed significant trends relative

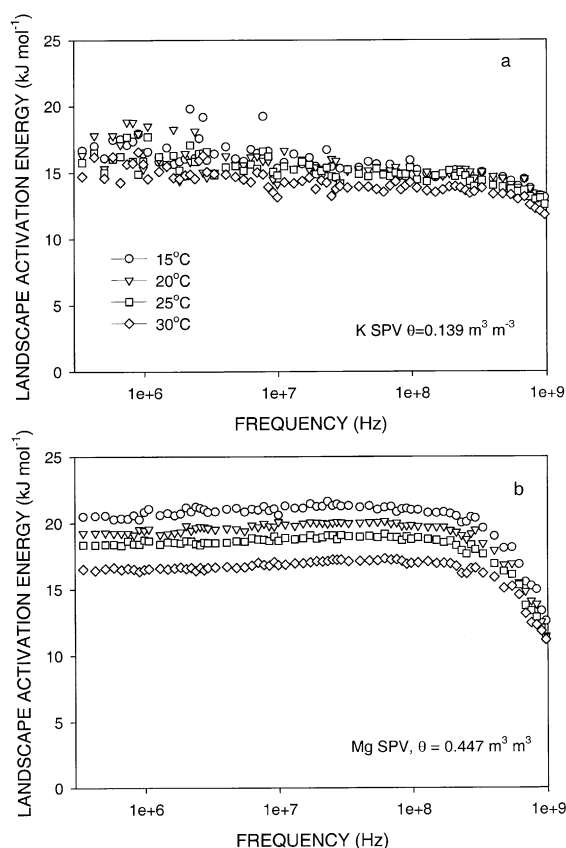


Fig. 3. Example landscape activation energy as a function of frequency and decreasing temperature for (a) a sample showing a decrease with frequency at lower frequencies, and for (b) a sample showing an increase with frequencies at lower frequencies.

Table 2. Cation and smectite main effects on calculated activation energies.

Activation energy	Cation			
	Ca	Mg	Na	K
	kJ mol ⁻¹			
Electrical conductivity	14.0 c†	22.3 c	11.4 c	29.6 c
Slope change frequency	19.9 b	29.8 a	19.9 b	25.6 a
Landscape‡	17.4 b	20.9 a	17.3 a	17.1 b
	Smectite			
	SPV	Otay	Hect.	IMV
Electrical conductivity	27.9 a	18.5 a	14.3 b	15.3 b
Slope change frequency	25.6 a	21.5 b	19.3 c	22.2 b
Landscape	18.5 b	18.0 c	16.9 d	19.2 a

† Means in the same row followed by the same letter are not significantly different at $p = 0.05$.

‡ The landscape values are the means for 20 and 25°C (midrange of data).

to the type of saturating cation (Table 2). The trends, however, were not consistent with either valence or hydration energy for the cations, although the results appear to be related to the combined effects of water content and cation hydration energy. The K-saturated samples had high activation energies because of the low water content, which increased tortuosity. The Mg-saturated samples also had high activation energies even though water contents were high; however, Mg is a strongly polarizing cation with high hydration energy that may hinder water and proton mobility. The Na- and Ca-saturated samples had lower activation energies because water contents of the samples were higher and hydration energies of the cations were lower.

When averaged across cations and water contents, the activation energies showed inconsistent trends with the type of smectite (Table 2) that appear to reflect both the total amount of water and the distribution of water between internal and external surfaces on the clays. The Hectorite had low activation energies because the Hectorite samples have high water contents. The SPV also has a high water content but had high activation energies because most of the water in the SPV was internal water rather than on the external surfaces. The Otay had intermediate to low activation energies because the Otay had low overall water contents.

The mean activation energies (across cation and smectite type) calculated from electrical conductivity showed an increase as water content decreased, but there was a lot of scatter with an adjusted r^2 of only 0.145 (Fig. 4). The activation energy calculated from the slope change frequency also increased significantly as water content decreased, but the adjusted r^2 was only 0.090. The landscape activation energy did not change significantly with water content. The mean activation energies calculated using the slope change frequency, were similar to landscape activation energies, but offset 3.28 kJ mol⁻¹ higher (Fig. 5) using the NLIN regression procedure of SAS.

Comparison with Literature

Calvet (1972, 1975) observed activation energies due to the electrical conductivity that ranged from 24 to 42 kJ mol⁻¹ for Mg-montmorillonite and from 29 to 39 kJ mol⁻¹ for Ca-montmorillonite. In both cases the activation energy increased with water content, opposite of

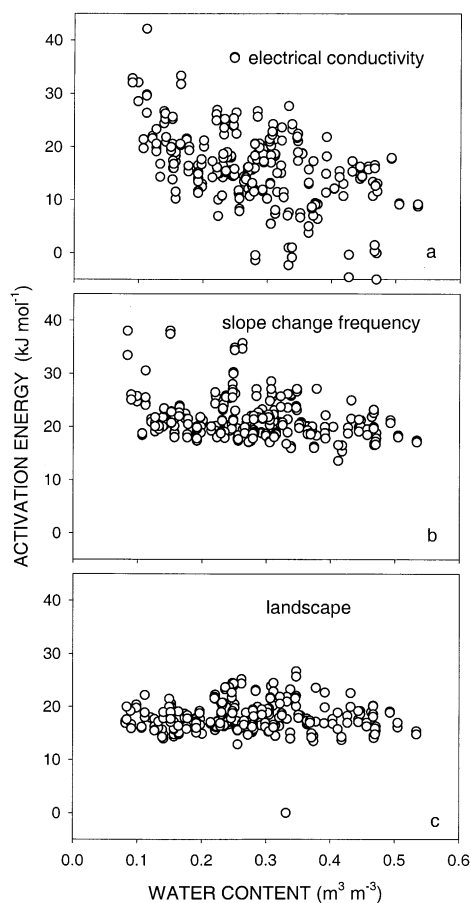


Fig. 4. Activation energies as a function of water content.

the trend in our data in which the activation energy decreased with increasing water content. Also his values were larger than our values. He did not show a distinct difference between Mg and Ca saturation, but we observed that Mg-saturated clays had significantly larger E_p from electrical conductivity than Ca. We expect the activation energy to increase at lower water contents because of greater tortuosity for charge carrier movement.

Calvet (1972, 1975) observed relaxation frequency activation energies ranging from 70 to 90 kJ mol^{-1} for Mg-montmorillonite, and from 80 to 105 kJ mol^{-1} for Ca-montmorillonite. These values are much larger than for our data. He observed higher relaxation E_r for Ca than for Mg-montmorillonite, but we observed larger E_r for Mg- than for Ca-smectites. Dudley et al. (2003) observed relaxation E_r 's ranging from 13 to 20 kJ mol^{-1} for Na-montmorillonite, and 18 to 28 kJ mol^{-1} for Ca-montmorillonite. These values are in the range of what we observed. It should be mentioned that Calvet (1972, 1975) used an indirect method (calorimeter), and only obtained ϵ'' (not ϵ') as a function of T (not f).

CONCLUSIONS

From our investigation of the effects of temperature on the electrical properties of smectites we conclude that the complex dielectric and electrical conductivity

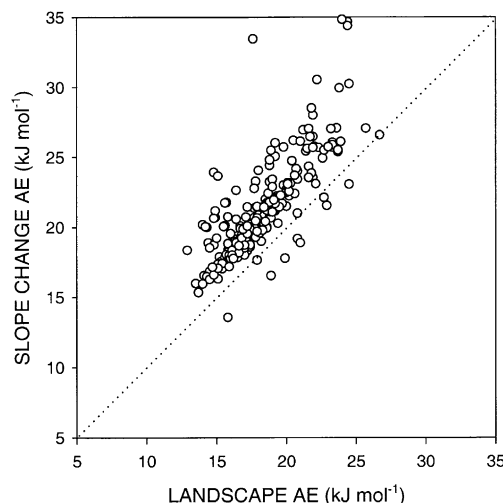


Fig. 5. Comparison of activation energy determined from the slope-change frequency with the landscape activation energy.

values decreased as temperature decreased, but trends for relaxation frequencies were less consistent. Although the total water content was constant, because the samples were in sealed cells, the water may have move from outside of the quasi-crystals into interlayer areas as the samples were cooled and out of the interlayers as the samples were heated (Kittrick, 1969). We were not able to verify this for our samples. Since water distribution in our samples might have changed with temperature, the effects of temperature might not be solely related to activation energies for electrical properties.

The temperature effects on the landscape E_{app} showed that the hydrated smectites did not behave according to dominant molecular relaxation mechanisms. Increasing system entropy over time and thermal treatments likely caused the increasing E_{app} . Migration of water in and out of smectite interlayers could impact water storage and release as well as particle orientation.

The three different methods of calculating activation energies did not always give the same trends for cations and smectites, but activation energies calculating using the slope change frequency and landscape activation energies were correlated. Generally K- and Mg-smectites had high activation energies and Ca- and Na-smectites had low activation energies. These results were influenced by both the amount of water present in the sample and by the hydration energy of the cation. The influence of different smectites on activation energies was affected by the relative amounts of water present in interlayers and external positions.

Our examination of the effects of different cations, water content, temperature, type of smectite, and frequency on the complex electrical properties of humidified clays has demonstrated that all of these variables influence the electrical properties and that there are substantial interactions. Because of the frequency-dependence, measurements at any one frequency are not easily reproducible nor easily interpreted. And because of the interaction between frequency and temperature, no simple equation will correct for temperature effects. Furthermore our results showing that E_{app} increased dur-

ing both heating and cooling cycles demonstrates that entropy changes in a soil induced by thermal cycling can impact electrical properties. Thus we conclude that simple one frequency measurements of permittivity or bulk electrical conductivity, as are commonly used to determine soil water content and salinity, are subject to potentially significant errors arising from interactions involving soil clays. We also conclude that these errors cannot be easily corrected with simple linear corrections for temperature and/or clay content.

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